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THE MOLECULAR GEOMETRY OF PYRAZINE IN
THE LOWEST TRIPLET STATE FROM PMDR
SPECTROSCOPY

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TRIPLET STATE FROM PMDR SPECTROSCOPY

by

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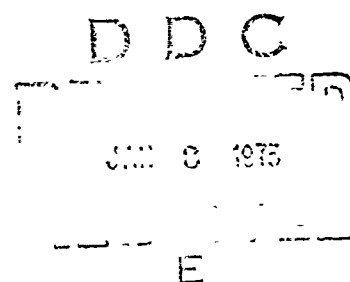
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THE MOLECULAR GEOMETRY OF PYRAZINE IN THE LOWEST

TRIPLET STATE FROM PMDR SPECTROSCOPY

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ABSTRACT

The triplet spin sublevel origins of the bands in the phosphorescence of pyrazine in a para-dioxane host are assigned using phosphorescence-microwave double resonance techniques. The assignments cannot be interpreted in terms of a D_{2h} structure for the molecule in the triplet state, and indicate a triplet state molecular symmetry of C_{2h} or lower.

INTRODUCTION

There have been strong indications from the structure of the absorption[1,2] and emission spectra that the molecular symmetry of pyrazine in the phosphorescent[3] n,π^* state is lower than D_{2h}. The instability of the D_{2h} structure in the triplet state has been interpreted[3] in terms of a pseudo-Jahn Teller vibronic coupling in the triplet manifold, and the appearance of multiple quanta of nontotally symmetric modes in the phosphorescence spectrum is apparently a manifestation of such vibronic coupling. The 937 cm^{-1} band, assigned[4] as $b_{1g}(\nu_{10a})$, is intense and also appears in two quanta. This is believed[3] to be due to vibronic perturbation of $^3B_{3u}$ (n,π^*) by $^3B_{2u}$ (π,π^*) along the b_{1g} normal coordinate. The second prominent nontotally symmetric mode in the phosphorescence is the 760 cm^{-1} band, assigned[4] as $b_{2g}(\nu_5)$, which also appears in two quanta, and is interpreted as arising from vibronic mixing between $^3B_{3u}$ (n,π^*) and $^3B_{1u}$ (π,π^*) via the b_{2g} mode.

The utility of phosphorescence-microwave double resonance spectroscopy[5] in investigating the molecular symmetry in the triplet state has been previously demonstrated in applications to benzene,[6] dibromonaphthalene,[7] tetrachlorobenzene,[8] and hexachlorobenzene.[9] The system investigated here is a 10^{-3} M solution of pyrazine in a para-dioxane host. The phosphorescence spectrum at 1.6°K is very sharp with an origin at 26410 cm^{-1}, and two prominent nontotally symmetric vibrations displaced by 760 cm^{-1} and 937 cm^{-1} from the 0,0 band. The designation of the spin origins of these bands can be used to deduce the symmetry of the molecule in the triplet state. Two methods which are complementary to each other are used to determine the origins of the bands: (1) analyzing the decay curves of the bands; and (2) microwave saturation of the zerofield transitions. Microwave-induced delayed phosphorescence (MIDP) techniques[10] in the latter is preferable to c.w. PMDR since the signal is enhanced, and also because uncertainties as to the relative populations of the spin states are eliminated.

EXPERIMENTAL

The experiments were performed on a solution of 10^{-3} M pyrazine in para-dioxane at 1.6°K. The pyrazine, obtained from the Aldrich Chemical Company, was vacuum sublimed and the middle fraction retained. The purity of the para-dioxane (Mallinckrodt Chemical Company) appeared to be adequate, on the basis that no impurity emission was detected. The samples were flushed with helium several times and then sealed under a low helium pressure in quartz ampules. The polycrystalline sample was excited by the 3130 Å line from a high pressure mercury arc which was isolated by an aqueous solution of 0.2 grams/ℓ K_2CrO_4, and a UG-11 glass filter. The spectrum was obtained on a Jarrell-Ash grating spectrometer with 50 slits, and the phosphorescence emission detected using an EMI-625GS photomultiplier tube. The phosphorescence decays and PMDR signals were collected on a TMC-401C CAT. The microwave source used was a Hewlett-Packard 8690B sweep oscillator with appropriate plug-ins.

RESULTS

Three zerofield transitions were detected at microwave frequencies of 9.886, 9.584 and 0.30 GHz. The transitions may be assigned to $|D| + |E|$, $|D| - |E|$ and $2|E|$, respectively. The ordering of the energies of the magnetic sublevels is fairly well established, having been determined by a variety of methods, including high-field optical detection,[11] low-field and zero-field optical detection,[12,13] and low-field Zeeman studies.[14] These studies were unanimous in assigning the ordering: $E(\tau_y) < E(\tau_z) < E(\tau_x)$ for the axis system where z is along the N-N axis, y is the other in-plane axis and x is normal to the plane of the molecule.

MIDP experiments reveal that depopulation of the triplet occurs predominantly through τ_y with a rate constant $k_y = 154$ sec^{-1}. The rate constants for the dark levels are $k_x = 5$ sec^{-1} and $k_z = 2.5$ sec^{-1}.

The decays of the 0,0, 760 cm^{-1} and 930 cm^{-1} bands were obtained at

1.6°K (Fig. 1). Three components could be extracted from the total decay, with
lifetimes: 6 msec, 200 msec and 400 msec, in agreement with MIDP results
where they were assigned to the lifetimes of τ_y, τ_x and τ_z, respectively. The de-
cay of both the 0,0 and 760 cm^{-1} bands could be resolved into three components,
which indicates that they originate from all three spin levels, assuming
that the spin-lattice relaxation is frozen at 1.6°K.[15] The 937 cm^{-1} band
decays primarily with the medium lifetime, with very little short or long
components, and hence may be assumed to originate from τ_x with little con-
tribution from τ_y and τ_z.

Table 1 shows the signs of the MIDP signals. After an appropriate
delay time (30-60 msec) between the shutting-off of the exciting light
and the start of the microwave sweep, $N_y(t) << N_x(t)$, $N_z(t)$ (where N represents
the population density of the spin level), and the sign of the microwave
signal immediately indicates the spin sublevel origins of the band. From
the table it may be concluded that both the 0,0 and 760 cm^{-1} bands originate
predominantly from τ_y. The 937 cm^{-1} band originates from both τ_y and τ_x.
However, τ_x contributes more to the intensity than does τ_y since the band
intensity decreases when D+E is saturated, after τ_y is allowed to decay.
The 847 cm^{-1}, 1519 cm^{-1} and 1861 cm^{-1} bands, like the 0,0, all originate
mainly from τ_y. The results of c.w. PMDR are also shown in Table 1. It is
interesting to note that the 760 cm^{-1} band does have a component originating
from one of the top levels. Table 2 shows the experimentally determined spin
sublevel origins of some representative phosphorescence bands.

DISCUSSION

For the axis system where x is normal to the molecular plane and z
passes through the nitrogens, the spatial symmetry of the lowest triplet
state in D_{2h} is B_{3u}. For this point group the 0,0 is predicted to originate
from τ_y and τ_z. This is in conflict with the observation that the 0,0 decay

has three components. It is noteworthy that time-resolved measurements of the polarization reveal[16] that all three spin states of the triplet contribute to the intensity of the 0,0 band in the emission of pyrazine in durene or p-dichlorobenzene hosts. Furthermore, Hall, Leung and El-Sayed[13] have shown that the dark level in D_{2h} has a slightly shorter lifetime than the spin level from which emission is allowed by symmetry, but not involving one center spin-orbit coupling terms. Generally,[7] the 937 cm^{-1} and 760 cm^{-1} bands are assigned to $b_{2g}(\nu_5)$ and $b_{1g}(\nu_{10a})$, respectively. Zalewski[4] reverses this assignment, designating the 760 cm^{-1} band as ν_5 and the 937 cm^{-1} band as ν_{10a}. In D_{2h}, bands of b_{2g} symmetry are predicted to originate from a single level, τ_y, which, assuming the first assignment to be the correct one, would be in conflict with the experimental result that the 937 cm^{-1} band originates from at least two spin levels. The 760 cm^{-1} band is predicted to originate from τ_z, while the experimental results reveal that it originates predominantly from τ_y with some contribution from τ_x. Assuming Zalewiski's assignment to be correct, the predicted origin of the 760 cm^{-1} band agrees with the observed origin (τ_y), but the 937 cm^{-1} band is expected to originate from τ_z, in conflict with experiment. These conclusions regarding the 937 cm^{-1} and 760 cm^{-1} bands are valid, regardless of whether the spin-lattice relaxation is frozen, since they are not derived from the decays as in the case of the 0,0. The experimental results, therefore, cannot be adequately interpreted in terms of a D_{2h} structure. Furthermore, the symmetry reduction is not exclusively crystal field induced since the vibronic bands reflect a non-D_{2h} symmetry.

A plausible distortion would be to a C_{2v} boat structure. The 0,0 in C_{2v} originates from the lower two spin levels (Table 3), again, in conflict with the experimental results based on the decay of the 0,0 band. The predicted origin of the 937 cm^{-1} band agrees with experiment, only if it is assumed that Zalewski's assignment is the correct one. However, the C_{2v} structure

may be ruled out on the basis of the predicted origins of the 760 cm^{-1} band which is in conflict with experiment, irrespective of whether it is assigned to b_1 (b_{1g} in D_{2h}) or b_2 (b_{2g} in D_{2h}).

The experimental results, however, do not conflict with a symmetry of C_{2h} or lower symmetry, where the bands are predicted to originate from all three spin levels.

The prominance of b_{1g} and b_{2g} vibrations is actually consistent with a C_{2h} structure. The 760 cm^{-1} vibration (b_{1g}, ν_{10a})[17] for example, involves an out-of-plane displacement of the hydrogens such that the two hydrogens on one side of the N-N axis move in the same direction but opposite to the direction in which the hydrogens on the other side of the N-N axis move. Thus strong vibronic coupling along the b_{1g} coordinate could result in a permanent distortion to C_{2h} if the crystal field is anisotropic, favoring one conformation over the other. The 930 cm^{-1} vibration (b_{2g}, ν_5)[17] involves opposite displacement of the hydrogens on one side of the N-N axis such that there is a reflection plane containing the N-N axis and the axis normal to the molecular plane. Strong vibronic coupling in this case would also result in distortion to C_{2h}, although the structure in this case will not be the same as that induced by the b_{1g} vibration. Which of the two forms is more stable will obviously depend on the difference in the strength of the vibronic coupling between the $^3B_{3u(n,\pi^*)}$ and the $^3B_{1u(\pi,\pi^*)}$ or $^3B_{2u(\pi,\pi^*)}$ states as well as the difference in energy between the coupled states. The role of the crystal field in stabilizing the distorted form is apparently the reason for the observed sensitivity of the zerofield transition frequencies to the host crystal field. It might also be suggested that the sensitivity of the zerofield transitions of pyrazine and pyrimidine to solvents might reflect the sensitivity of the type of the frozen geometry of the molecule as well as the difference in the energy of the coupled states to the host crystal field. Spin orbit coupling between these states could also contribute to the zerofield splittings of the $^3B_{1u(n,\pi^*)}$ state. This contribution is also sensitive to the solvent, which determines the relative energies of these states as well as the type of distortion. This could also be an added reason for the sensitivity of the zerofield splittings of pyrimidine and pyrazine to the

ACKNOWLEDGEMENTS

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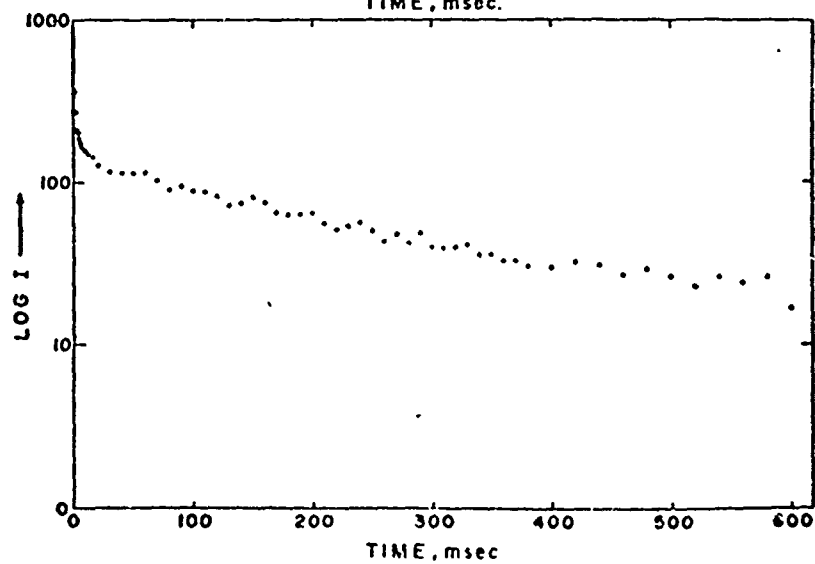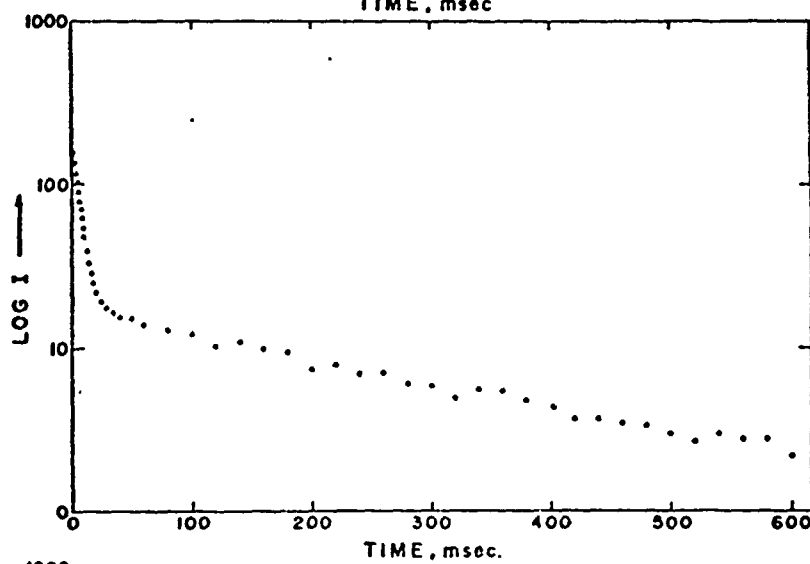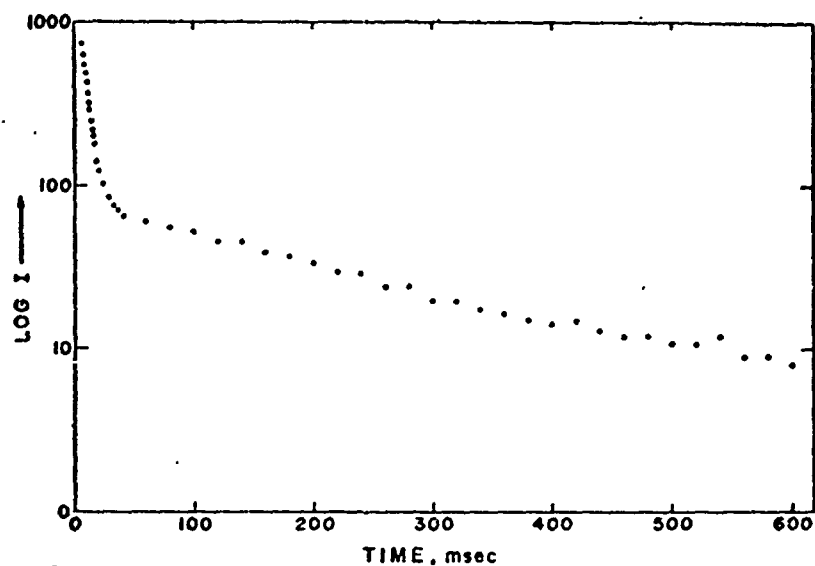17. K. K. Innes, J. Mol. Spectry. 22, 125 (1967).

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FIGURE CAPTIONS

Figure 1. The decays of the 0,0 (top), 760 cm^{-1} (middle), and 937 cm^{-1} (bottom) bands.

Figure 2. The $|D| + |E|$ and $|D| - |E|$ MIDP signals for the 760 cm^{-1} (top) and 937 cm^{-1} (bottom) bands. The microwave frequency is 9.4 GHz at t = 0, and the sweep rate is 1.7 Mc/sec.
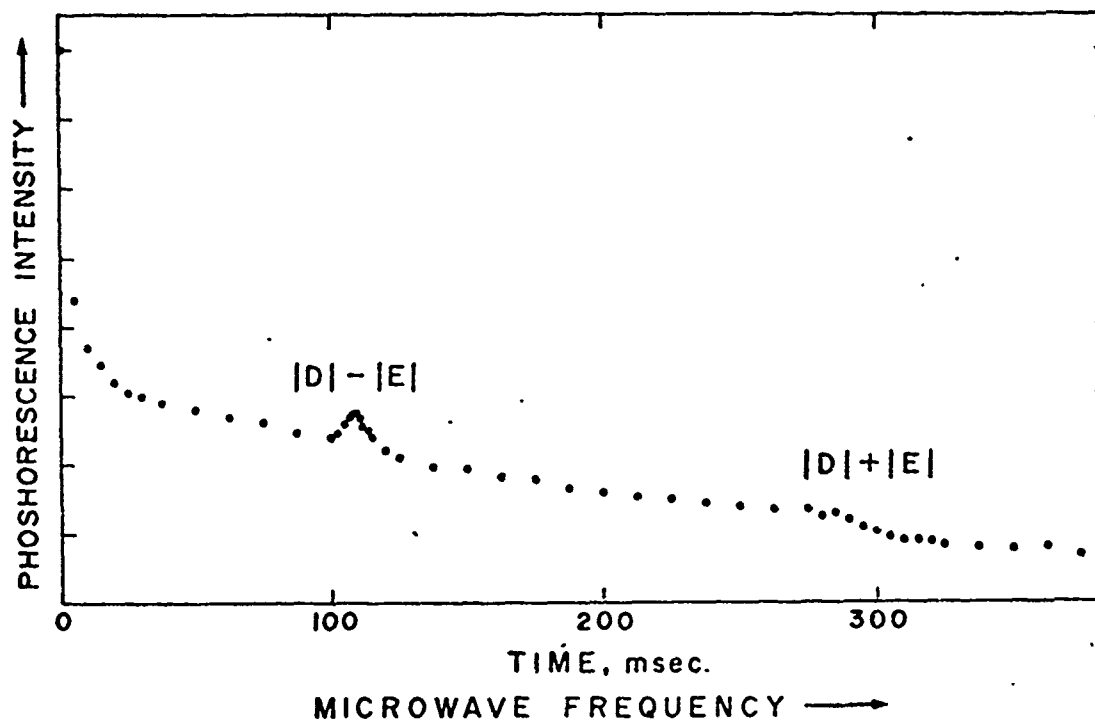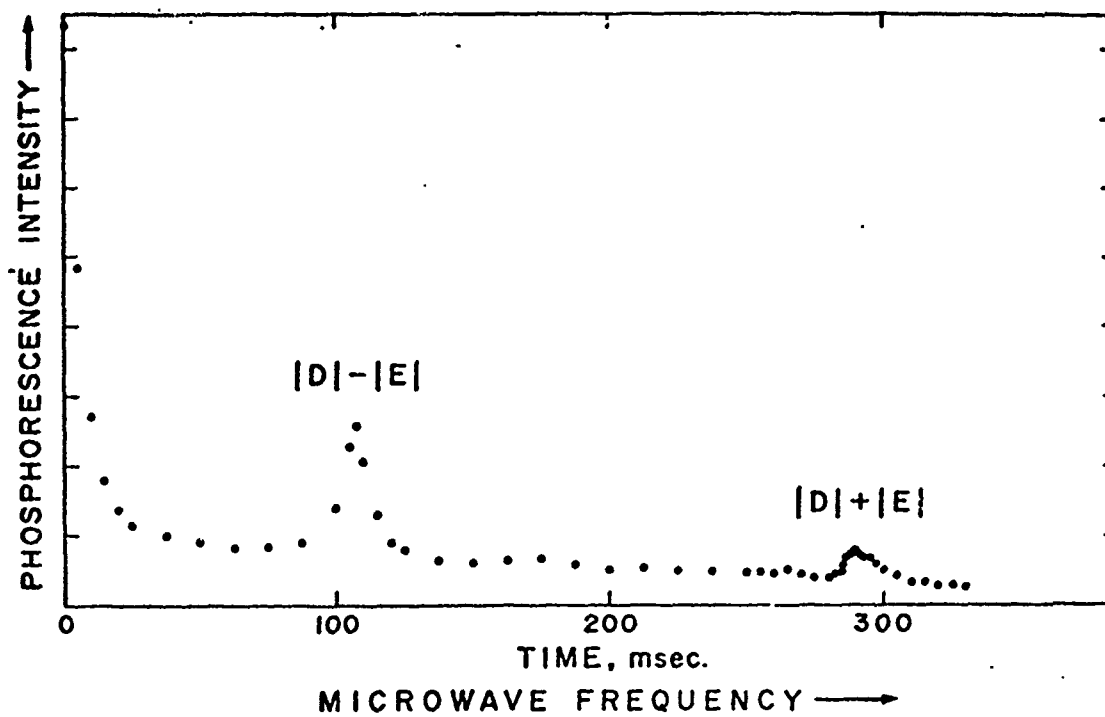
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Figure 1

Figure 2

TABLE 1

Signs of PMDR Signals of Representative

Bands in the Phosphorescence of Pyrazine

$\lambda, \overset{\circ}{A}$	$\Delta v \ cm^{-1}$	Sign of PMDR Signal			
		Chopped Excitation		c.w. Excitation	
		D + E	D - E	D - E	2E
3785.3	0	+	+	+	0
3888.4	700.3			+	0
3897.5	760.3	+	+	+	+
3910.7	846.9	+	+	0	0
3924.5	936.8	-	+	0	+
4016.3	1519.0	+	+	+	0
4018.4	1532.0			0	-
4072.1	1860.7	+	+	+	0

TABLE 2

The Experimentally Determined Relative Contributions of the Spin Components to the Band Intensity

λ (air) Å	ν (vac.) cm⁻¹	Δν cm⁻¹	I (rel.)	Assignment (17)	I (rel.) of Spin Component		
					τ_y	τ_z	τ_x
3785.3	26410.5	0	vs	0,0	s	w	w
3888.4	25710.2	700.3	vw	$\nu_4(b_{2g})$	m	w	s
3897.5	25650.2	760.3	w	$\nu_{10a}(b_{1g})$	s	w	s
3910.7	25563.6	846.9	vw	$2\nu_{16b}(2b_{3u})$	s	w	w
3924.5	25473.7	936.8	vw	$\nu_5(b_{2g})$	m	w	s
4016.3	24891.5	1519.0	m	$2\nu_{10a}(2b_{1g})$	s	w	w
4018.4	24878.5	1532.0	vw	$\nu_{8b}(b_{3g})$	w	s	w
4072.1	24549.8	1860.7	s	$2\nu_5(2b_{2g})$	s	w	w

I (rel.) = relative intensity

vs, s, m, w, vw = very strong, strong, medium, weak, very weak

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TABLE 3

Correlation of the Species and the Predicted Sublevel Origins of the Bands for D_{2h} and its Subgroups

D_{2h}		$C_2(x)$ C_{2v}		$C_2(y)$ C_{2h}		$\sigma(yz)$ C_s	
Species	Origins	Species	Origins	Species	Origins	Species	Origins
a_g	τ_y, τ_z	a_1	τ_y, τ_z	a_g	τ_x, τ_y, τ_z	a'	τ_x, τ_y, τ_z
b_{1g}	τ_z	b_1	τ_y, τ_x	b_g	τ_x, τ_y, τ_z	a''	τ_x, τ_y, τ_z
b_{2g}	τ_y	b_2	τ_z, τ_x	a_g	τ_x, τ_y, τ_z	a''	τ_x, τ_y, τ_z

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